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(94) Phosphoric acid crystallization process.

(97) The present invention discloses a new method for obtaining a crystallized phosphoric acid of relatively high purity starting with conventional phosphoric acid. The new method is based on crystallization of orthophosphoric acid hemihydrate from the phosphoric acid. Massive nucleation which would lead to the formation of unprocessable masses is avoided in the new method by providing unusually large amounts of fine relatively pure seed crystals of orthophosphoric acid hemihydrate and operating the crystallization process under conditions which favor crystal growth on the seed crystals and disfavor the occurrence of secondary nucleation. To prevent the crystallizing magma from reaching a viscosity which would render further processing difficult the present invention provides for recycling raffinate in an amount sufficient to maintain the solids content of

the crystallizing magma below about 40%.

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Phosphoric Acid Crystallization Process

Field of the Invention

This invention relates to the production of purified phosphoric acid and, in particular, to the production of concentrated high-purity phosphoric acid.

The Prior Art

Most of the high-purity phosphoric acid on the market today is produced by the so-called furnace process, which involves the production of elemental phosphorus in an electric furnace from phosphate rock and coal. The elemental phosphorus is then burned and the resulting phosphorus pentoxide is hydrolyzed to high purity phosphoric acid. This technology is generally costly and very energy intensive. Efforts have been made in the past to develop technology for the production of high-purity phosphoric acid from impure acids, such as wet-process acid. Wet-process acid is produced via the acidulation of phosphate rock with sulfuric acid, and is less expensive to make. Such acid, however, is contaminated with significant concentrations of numerous impurities, such as iron, aluminum, magnesium, sulfate, fluorine and silica. Other impure acids with similar impurities are available "spent acids", that is, acids which, regardless of their original manufacture or purity, e.g., furnace process or wet-process, have been used ("spent") in such industrial applications as metal finishing or in catalyst applications.

While crystallization of the phosphoric acid would normally be considered as a process which would result in a crystallized product of relatively high purity (leaving behind a raffinate containing the rejected impurities), crystallization has not been practiced on an industrial scale for purifying wet-process acid, or for purifying other impure acids. Apparently crystallization has not been commercially accepted because of great difficulty in controlling the rate of crystallization. When the impurities normally associated with wet-process or spent acids are present, the impure acid can withstand very substantial cooling, well into the supersaturation region, before crystallization occurs. Even then spontaneous crystallization can be an extremely slow process. However, once crystals are formed by spontaneous (primary) nucleation, or if seed crystals are added in amounts substantially lower than the amounts used in the method of this invention, the impure acid tends to crystallize relatively rapidly (presumably by secondary nucleation) to a putty-like intractable mass which has a viscosity typically in excess of 50,000 centipoises and which

cannot be further processed or separated. This rapid crystallization of phosphoric acid into a putty-like intractable mass is hereinafter referred to as "catastrophic crystallization".

A number of processes have been proposed for removing impurities from phosphoric acid by either extraction or crystallization. For example, U.S. Patent No. 3,642,439 describes an attempt to provide a process for upgrading the purity of wet-process phosphoric acid. In this process the inventors claim that magnesium can be selectively removed from the wet-process acid via the crystallization of magnesium-containing precipitates. The examples cited in the '439 patent indicate that the efficiency of the process is very limited. The magnesium content before the precipitation step in one of the examples was 0.4%, while after the crystallization and filtration the magnesium content of the purified acid was 0.2%. Thus, the process facilitates only the removal of about 50% of the magnesium content in the feed acid and does practically nothing to remove other impurities contained in the wet-process phosphoric acid.

U.S. Patent No. 4,299,804 describes another process for the removal of impurities from wet-process phosphoric acid by crystallization. In this case magnesium and aluminum impurities are claimed to be removed in the form of a magnesiumaluminum fluoride. Magnesium removal efficiencies of up to 90% are indicated by the examples; however, aluminum removal effectiveness is generally much poorer and the product still contains the other impurities such as iron, sodium, silica and fluoride. The examples indicate that the efficiency of the aluminum and magnesium removal process varies from sample to sample.

U.S. Patent No. 4,243,643 refers to another process for the removal of metallic ion impurities from wet-process phosphoric acid. This process also suffers from several distinct disadvantages. It requires the use of a precipitant comprising ions of calcium and fluorine to cause the precipitation of magnesium from the acid, and it requires that the sulfate concentration of the acid exceed 2%. Even then the effectiveness of the process is only of the order of about 50% for magnesium and even lower with respect to other metallic impurities present in the wet-process acid, such as iron, aluminum and sodium.

U.S. Patent No. 3,890,097 concerns a process for the purification of wet-process phosphoric acid which involves the crystallization from wet-process acid of a P_2O_5 -containing entity rather than of the impurities. This patent suggests the addition of a quantity of sulfuric acid to wet-process phosphoric

acid in an amount sufficient to raise the concentration of sulfuric acid in the solution to a range of from about 10% to 15% by weight. The '097 patent points out that crystallization of wet-process acid is impractical because of the low temperatures required and the high viscosities which occur. The addition of sulfuric acid to the impure phosphoric acid is claimed to lower its viscosity and increase its freezing point. The distinct disadvantage of this process lies in the need for the addition of costly sulfuric acid which is used to modify the physical characteristics, specifically the freezing point and the viscosity, of the phosphoric acid solution from which the purified material is crystallized. As a consequence of this sulfuric acid addition, the sulfuric acid content of the purified phosphoric acid is relatively high, that is, over 1% by weight, and the process is further burdened by a higher water content in the raffinate which carries about 50% of the original P_2O_5 values.

British Patent No. 1,436,115 also makes reference to crystallization in purifying wet-process phosphoric acid. In this patent, however, the need to first purify the wet-process acid by solvent extraction is stressed. The disclosure teaches that it is not in fact practicable to produce a purified phosphoric acid by direct crystallization from wet-process phosphoric acid. A similar opinion is expressed in U.S. Patent No. 3,912,803.

U.S. Patents No. 4,215,098 and 4,296,082 teach that crystallization of phosphoric acid is to be preceded by a purification step and offer heat treatment processes which serve to bring the phosphoric acid to a concentration about 78% P_2O_5 and precipitate dissolved impurities from the acid. Only then is the acid diluted and subjected to crystallization.

U.S. Patent No. 4,083,934 discloses a process for obtaining purified crystallized orthophosphoric acid from superphosphoric acid. The patent does not address the direct purification of wet-process phosphoric acid or the crystallization of phosphoric acid hemihydrate.

Japanese Patent No. 14,692, published in 1969, describes a process for purifying phosphoric acid by crystallization. In this patent the patentees point out that, although crystallization would be a desirable method for purifying phosphoric acid, it has not been employed industrially. Working from the assumption that it is the impurities which adversely affect the rate of crystallization, the Japanese patent describes a pre-crystallization process using oxidants which remove not only organic impurities but also inorganic impurities, such as calcium phosphate, calcium sulfate, chromium, vana-

dium and manganese, followed by further pre-processing to remove fluoride impurities. It is only after such pre-purification, according to this patent, that practical crystallization can be employed.

In the Proceedings of a Conference of Industrial Crystallization, published in 1976, Aoyama and Toyokura describe a process said to bring about crystallization of phosphoric acid from crude wet-process acid concentrated to about 60% P_2O_5 . Although the authors claim to have operated a pilot-scale crystallizer for as much as two weeks satisfactorily, nothing is said in the description as to conditions of seeding or control which would preclude catastrophic crystallization. As discussed below in the description of the present invention, it is the problem of catastrophic crystallization which the present invention overcomes by proper control of the seeding conditions. The only discussion of seeding in the Aoyama et al. paper refers to control of the circulation rates through different sections of the crystallizer, which are said to affect the number of seed crystals in the growing bed. However, the details of this control are not described. To the extent it is indicated in their process description it appears that the "seed" crystals are, in fact, products of primary crystallization of the wet-process phosphoric acid. In developing the method of the instant invention the inventors have found that such crystals, when used as the sole source of seed, do not provide controllable results.

An object of this invention is to provide a method for controlling the seeding and other conditions required to avoid catastrophic crystallization while crystallizing phosphoric acid. Another object is to provide a method for purifying phosphoric acid by means of crystallization without the need of solvent extraction techniques. Another object is to provide a process for the manufacture of high-purity phosphoric acid from wet-process phosphoric acid by the selective crystallization of phosphoric acid hemihydrate crystals from the impurities normally associated with the wet-process acid. Still another object of the present invention is to provide a method for purifying wet-process phosphoric acid by crystallization of its P_2O_5 entity without the continuous use of reagent additives. A further object of the invention is to provide a method for producing a purified phosphoric acid having a higher P_2O_5 concentration than the feed acid from which it is made. A still further object is to provide a process for manufacturing concentrated high purity phosphoric acid from wet-process phosphoric acid by means of selective crystallization of the P_2O_5 entity in the wet-process acid which process affords the flexibility of simultaneously manufacturing various purity grades of concentrated phosphoric acid products by means of remelting and recrystallizing said products.

Description of the Invention

In accordance with the process of this invention, impure phosphoric acid containing impurities which interfere with crystallization (such as wet-process phosphoric acid, spent acids from metal finishing operations and acids from spent catalysts) having a solids content below about 5% and preferably below about 3%, is subjected to crystallization under controlled conditions of agitation, temperature and crystal seeding. The acid is fed into an agitated crystallizer vessel, or series of such vessels, and maintained at a temperature between about -10° and 30°C, at which it is supersaturated with respect to phosphoric acid hemihydrate.

The feed acid should be sufficiently concentrated so that crystallization will occur within this temperature range. Normally this requires an acid containing over 50% P_2O_5 , and less than about 66% P_2O_5 (which corresponds stoichiometric $H_3PO_4 \cdot 1/2H_2O$).

The vessel, or vessels, should be sized so that the impure acid and seed crystals have a nominal residence time between about 30 minutes and 20 hours. If the process is carried out batchwise the calculation of residence time is straightforward. If the process is carried out in stirred vessels, with continuous addition of feed acid and continuous withdrawal of magma, nominal residence time refers to the volume of the vessel divided by the volumetric feed rate. Theoretically such a system will retain some portion of the feed for longer than the nominal residence time, and another portion for a shorter period.

The means of cooling may be indirect heat exchangers, direct injection of low boiling fluid or other cooling means common in industry.

Seed crystals of relatively pure orthophosphoric acid hemihydrate, $H_3PO_4 \cdot 1/2H_2O$ are introduced into the vessel or vessels in an amount sufficient to provide for crystallization without the development of a viscous, inseparable mass. Typically, the acid is seeded with crystal seeds in an amount of at least about 2% by total weight of the acid to be crystallized and, preferably, at least 5%. The amount of seeding required to avoid catastrophic crystallization varies with the degree of supersaturation of the acid. If the temperature of the system is only moderately below the saturation temperature, the amount of seed crystals required to prevent catastrophic crystallization will be less than the amount of seed crystals required if there is a high degree of supersaturation.

The seed crystals suspended in the phosphoric acid solution are then allowed to grow, while maintaining a temperature insuring supersaturation, to the point where the concentration of solids in the

resulting slurry, or magma, in the crystallizer reaches a level of between about 10% and 50% by weight. The crystallized product is then separated. Preferably, the slurry is fed to a centrifuge, or centrifuges, to achieve the desired separation of the solid and liquid phases. The liquid phase, or mother liquor, is a lower-grade P_2O_5 stream which carries the bulk of the impurities present in the feed phosphoric acid, such as iron, aluminum, magnesium, sulfate, silica, fluorine and calcium. The solids are the purified phosphoric acid product in the form of orthophosphoric acid hemihydrate, $H_3PO_4 \cdot 1/2H_2O$.

When the process of this invention is operated in a batch mode the seed crystals of the orthophosphoric acid hemihydrate are added at the beginning of the crystallization cycle in which a given batch of phosphoric acid is subjected to crystallization as already described. When the process is operated in a continuous manner, on the other hand, the seed crystals of orthophosphoric acid hemihydrate are introduced into the crystallization vessel continuously or intermittently in order to avoid catastrophic crystallization.

Theory of the Invention

While the present invention is not limited to any theory, an explanation of what the inventors believe happens is helpful to understanding the invention and its distinctiveness.

Crystallization processes, including the crystallization of phosphoric acid hemihydrate, generally involve both nucleation and crystal growth. In an idealized crystallization process these two mechanisms balance each other so that the rate of nucleation and the rate of crystal growth, both in response to supersaturation, provide a steady-state product of crystals of reasonable dimensions with the number of grown crystals withdrawn essentially equalling the number of new crystal sites generated by nucleation.

Two types of nucleation are generally recognized, viz. spontaneous (primary) nucleation and secondary nucleation. Spontaneous nucleation refers to that which occurs in the absence of seeding. Secondary nucleation refers to that which occurs in the presence of seeds or other crystals of the crystallizing material.

The inventors have observed that, when crystallizing phosphoric acid hemihydrate from wet-process acid, the impurities associated with the acid tend to inhibit spontaneous nucleation. Although other impure forms of phosphoric acid were not studied while making the present invention the impurities present in wet-process acid are known to occur in other impure acids such as spent acids from metal finishing operations, and spent acid

catalysts. Typically, a phosphoric acid, which contains such impurities, even when concentrated to as much as 63% P_2O_5 , will not spontaneously nucleate within a reasonable time at temperatures as low as -40°C . Based on equilibrium considerations, such an acid should begin to crystallize at about 5 -20°C . It is found in practice that concentrated impure phosphoric acid, at a temperature in the order of 0° -10°C will normally not crystallize even when subjected to agitation or impurity solids which will normally evoke nucleation in other supersaturated systems.

The inventors have observed also that the addition of a small amount of seed crystals of pure orthophosphoric acid hemihydrate to supercooled phosphoric acid will bring about relatively rapid crystallization, sometimes in less than an hour. This is probably due to secondary nucleation, which can proceed much more rapidly than either primary nucleation or crystal growth. However, the resultant crystallized mass is highly viscous and virtually inseparable, that is, it is virtually impossible to separate the hemihydrate crystals from the mother liquor. When such crystallization occurs, it is usually necessary to reheat the mass to a temperature sufficient to remelt the phosphoric acid in order to handle the material in a commercially practical manner.

The inventors believe that the occurrence of such catastrophic crystallization in phosphoric acid is due to an imbalance between nucleation and crystal growth such that once nucleation begins it tends to proceed rapidly relative to crystal growth to relieve supersaturation before substantial crystal growth occurs. The result is the formation of a viscous, intractable mass of extremely fine crystalites. In the present invention this catastrophic crystallization, which the inventors attribute to extensive secondary nucleation, is suppressed by providing unusually large amounts of relatively pure fine seed crystals and maintaining the degree of supersaturation low enough. The inventors hypothesize that this permits crystal growth to proceed sufficiently rapidly to relieve supersaturation before a substantial amount of nucleation occurs.

Description of the Principal Process Parameters

The phosphoric acid to which the present invention is applicable is the impure phosphoric acid containing impurities which interfere with crystallization. Such acids can be the ordinary wet-process acid of commerce, typically containing about 54% P_2O_5 or the spent acids such as mentioned above. However, the equilibrium freezing point of phosphoric acid hemihydrate from such acids is quite

low. For this reason, and to improve the process P_2O_5 yields, it is preferred to use an acid containing 58-63% P_2O_5 .

As used herein, " P_2O_5 yield" refers to the percentage of the P_2O_5 originally present in the acid fed to the crystallization step which reports in the crystallized phosphoric acid hemihydrate cake. As a practical matter, P_2O_5 yields lower than about 20% are considered of little or no interest from a process economics point of view. A preferred phosphoric acid starting material is that prepared in accordance with commonly-assigned U.S. Patent No. 4,487,750 issued December 11, 1984, to Astley et al. An acid prepared by diluting so-called superphosphoric acid, a commercially available product containing between 69 and 76% P_2O_5 , to the 58-63% P_2O_5 range is also suitable as a starting material.

It is also preferred that the starting material be substantially free of solid impurities before crystallization. Solids present in the starting acid used in the process of this invention may appear as contaminants in the crystallized product when the latter is separated from the raffinate. For that reason, the solids content of the feed acid should be less than 5%, and preferably less than 3%.

Certain impurities influence the process P_2O_5 yields, and can affect the equilibrium freezing point of phosphoric acid hemihydrate. It has been found, for instance, that the fluoride ion content affects the P_2O_5 yields in wet-process acids. Since wet-process phosphoric acid varies in its impurity content, it may be desirable for best P_2O_5 yields when dealing with wet-process acid to assure a fluoride content of at least 0.5% to 0.7%. Many wet-process acids naturally contain 0.7% to 0.9% fluoride. However some acids may be specially processed in ways which reduce the fluoride content, sometimes to as little as 0.2%. In such cases best results are obtained in practicing the present invention by adding enough hydrofluoric acid to increase the fluoride ion content to the range of 0.5%-0.7% for the first stage of crystallization.

In still higher concentration, the fluoride ion has even more beneficial effects. Again with reference to wet-process acid, fluoride ion has been found to permit crystallization under conditions which reduce the viscosity of the crystallizing magma at a given yield level if present in amounts between 1%-2%. Hence even in typical wet-process acid where the fluoride ion content may be between 0.7 and 1%, the addition of HF can have a beneficial effect on processing. Similar results are found when using fluosilicic acid.

at a suitable temperature with a paratus. The temperature should be maintained sufficiently low to assure a good yield of crystallized product. For instance, if the crystallizer is fed with a wet-process acid concentrate containing 61% P_2O_5 (equivalent to 84.25% H_3PO_4) and operated at a temperature at which the equilibrium freezing point concentration of P_2O_5 is 57% (equivalent to 78.73% H_3PO_4) the maximum P_2O_5 yield of orthophosphoric acid hemidhydrate (91.6% H_3PO_4) will be around 47%. If the temperature of the crystallizer is lowered the P_2O_5 yield will increase in accordance with the reduced equilibrium concentration of H_3PO_4 at such lower temperature. On the other hand, operation at too low a temperature relative to the saturation conditions can increase the degree of supersaturation sufficiently to give rise to secondary nucleation, a phenomenon which we desire to suppress. Therefore, the tem-

level sufficient to suppress secondary nucleation leads to a preferred embodiment of the present invention for maximizing P_2O_5 yield. In this preferred embodiment crystallization is carried out continuously in two or more stages, with magma withdrawn from each stage used or feed the next succeeding stage. Fresh feed is supplied to the first stage and product magma is withdrawn from the last stage. Each stage operates at a lower temperature than the immediately preceding stage. In this manner, the temperature in each stage can be controlled to suppress secondary nucleation, while on an overall basis the temperature can be lowered in the final stage sufficiently to provide a high P_2O_5 yield.

The crystallized $H_3PO_4 \cdot 1/2H_2O$ obtained by crystallization from wet-process phosphoric acid is substantially purer than the wet-process acid before crystallization. The improvement in purity can be illustrated by the typical data shown in the Table I, below:

TABLE I
Product Purity From Wet-Process Acid

	<u>Wet-Process</u>	<u>Crystallized Product Cake</u>
P_2O_5	59.6%	64.6%
SO_4	3.5	0.16
Fe_2O_3	1.7	0.22
Al_2O_3	1.6	0.14
F	0.9	0.08
MgO	0.7	0.04
Carbon	0.2	0.04

For some applications the first-crop product may be sufficiently pure. However it is still quite discolored and insufficiently purified for many purposes. The firstcrop product can be further purified by washing and/or secondary crystallization. Thus, for example, washing of the first-crop product followed by heating will cause it to melt at around 25-

30°C. The melted material can then be cooled, reseeded, and recrystallized. The product of the secondary crystallization can be washed and/or remelted and recrystallized to obtain a tertiary product, if desired. The improvement in purity resulting from such second and third crystallization is illustrated by the data shown in Table II, below:

TABLE II

Effect of Recrystallization on Product Purity

	<u>Wet-Process Acid</u>	<u>Product Cake of Primary Crystallization</u>	<u>Product Cake of Secondary Crystallization</u>	<u>Product Cake of Tertiary Crystallization</u>
P ₂ O ₅	60.8%	64.3%	64.6%	64.9%
Fe ₂ O ₃	1.89	0.3	0.06	0.01
Al ₂ O ₃	2.07	0.3	0.05	0.004
MgO	0.91	0.16	0.02	0.001
SO ₄	4.30	0.67	0.14	0.05
F	.87	0.1	0.01	0.01
Carbon	0.2	0.04	0.01	0.006

The tertiary acid has a purity and color suitable for many applications.

The selection of seed crystals is a third important process variable. Seed crystals used in the present invention should be fine, relatively pure and used in a sufficient quantity that supersaturation will be relieved by crystal growth before a significant amount of secondary nucleation occurs.

In the early tests of the present invention, we found that fine crystals of H₃PO₄•1/2H₂O obtained by adding a small amount of seed to a supersaturated solution of reagent grade phosphoric acid gave excellent results. This provided seeds which were of high purity and small size, i.e., in the order of 0.12 mm in the longest dimension. We have also found that wet-process phosphoric acid which has been crystallized at least twice will yield good seed crystals. On the other hand, we have found that relatively impure crystals at seed crystal addition rates of 8% to 15%, are relatively less effective to produce good results, even if fine in particle size. We have observed, for example, that good results are obtained when the seed crystals of H₃PO₄•1/2H₂O contain less than 0.1% iron (as Fe₂O₃) and have a crystal length of less than 0.3 millimeter. Also, the acid from which the seeds are made should preferably have a P₂O₅ concentration of between 58% and 63%.

Seed crystals may be conveniently generated on batch basis as described above. Such seed is largely composed of material resulting from secondary nucleation with little opportunity for crystal growth. If such a batch of seed is kept insulated, it can be used from time to time as needed. Seed crystals can also be prepared by a method such as described in copending application No. (Agents' ref.: BO 33854) of April 25, 1986. Thus, for

example, a seed crystal generator has been designed to which fresh, cold acid is supplied continuously, and the residence time in the generator is limited so that the seed is formed largely by rapid nucleation before there is a significant opportunity for crystal growth.

An important aspect of the present invention relates to the amount of seed added. That amount should be sufficient to preclude massive or catastrophic crystallization which, as already mentioned, results in a viscous mass in which the phosphoric acid hemihydrate crystals cannot be separated from the mother liquor. As explained above, we believe that the occurrence of such catastrophic crystallization is the result of secondary nucleation which is not adequately suppressed.

In continuous processing, seed may be added periodically or continuously; however, if it is added periodically, the frequency should be sufficient to maintain crystal growth at a rate which will prevent catastrophic crystallization. When in a continuous crystallization mode, crystal production may not be self sustaining without seed crystal addition. We have observed that in such continuous operation if seeding is suspended, crystallization will either cease, or catastrophic crystallization will ensue.

The amount of seed required to afford controlled crystal growth is dependent upon the amount of supersaturation of the solution being recrystallized, the size of the seed crystals and seed crystal purity. In a typical case, a wet-process phosphoric acid of about 60% P₂O₅ is cooled to between 0° and 5°C in the crystallizer. In such a system we use at least 2% seed crystals based on the weight of crude acid, and typically we provide about 5% fine, high-purity seed crystals. The

TABLE IIIEffect of Seed Addition

<u>Test No.</u>	<u>Temperature</u>	<u>% Seed</u>	<u>Seed Origin</u>	<u>P₂O₅ Yield</u>	<u>Comments</u>
1	4°C	5	Furnace Acid	44%	Easy separation
2	4°C	3	Furnace Acid	33%	Easy separation
3	4°C	2	Furnace Acid	30%	Easy separation
4	4°C	1	Furnace Acid	16%	Viscous, difficult separation
5	4°C	5	Product from Test 1	13%	Viscous, difficult separation
6	4°C	1	Product from Test 1	3%	Viscous, difficult separation

In the foregoing table the furnace acid seed crystals were of a size in the order of 0.1 mm long. The crystals used for seeding in Tests 5 and 6 were those obtained in Test 1. These crystals were longer than 0.3 mm.

As can be seen from the above data the best results were obtained when the wet-process acid was seeded with furnace acid seeds in amounts substantially higher than 1% by weight of wet-process acid.

In carrying out crystallization in stages, as suggested above, the viscosity of the magma can become quite high as crystallization progresses, particularly at lower temperatures, even in the absence of catastrophic crystallization or secondary nucleation. Magmas having excessively high viscosities, for example over 30,000 centipoises, become very difficult to process. Larger amounts of energy are required to maintain agitation, pumping

costs increase, and separation of the product from the magma derived from the last stage by filtration or centrifuging becomes more difficult. It is desirable therefore to maintain viscosity below about 30,000 centipoises, and preferably below 10,000 centipoises. In accordance with a preferred aspect of the invention, it has been discovered (see co-pending application No. (see agents ref.: BO 33855) dated April 25, 1986), that raffinate obtained from the magma derived from the final stage can be recycled to the crystallizers to reduce the viscosity therein. In accordance with this related invention, raffinate is recycled in an amount sufficient to maintain the crystallizing magma within an acceptable viscosity range. Usually, this will be when the crystallizing magma contains less than 40% solids. This expedient is particularly desirable in staged separations.

The present invention was tested using the apparatus illustrated in the figure. The apparatus consisted of three successive crystallizers 1, 2 and 3 of approximately 5 gallons each. Each crystallizer was provided with an overflow spout (respectively 4, 5 and 6) with the final product overflow from crystallizer 3 entering a magma collection vessel 7. The magma in vessel 7, consisting of a mixture of crystallized phosphoric acid and raffinate, was separated into its components by a centrifuge in a separate step (not shown). Drum 8 of phosphoric acid which had previously been concentrated to approximately 60% P_2O_5 , were used to supply feed which was pumped by feed pump 9 through feed supply line 10 into crystallizer 1.

Each crystallizer was fitted with a spiral stainless steel tube (indicated by fragments 12, 13, and 14) which maintains the temperature of the respective crystallizing containers. Each of the cooling coils was fitted with coolant supply and return lines 15, 16 and 17 connected to a common coolant supply (not shown). Each crystallizer was also fitted with an agitator driven by an electric motor (18, 19 and 20).

In the operation of the staged crystallizer shown in the drawing it was found that the viscosity in the second and third stages had to be controlled. Excessive viscosity was noted when the current required to operate the stirrers 19 and 20 in these two stages became excessive. To avoid excessive viscosities, provision was made to recycle raffinate obtained from the centrifugation of the magma accumulated in vessel 7 from one or more preceding centrifugations. Such raffinate was stored in a raffinate cooling tank 24 provided with a cooling coil - (fragments 25 shown) and a stirrer driven by electric motor 26. The cooling coil 25 was provided with coolant from the same common cooling source previously referred to through coolant supply and return lines 27. Raffinate was pumped to each of the second and third stages by raffinate recycle pumps 30 and 31 through raffinate supply lines 32 and 33.

Seed crystals were supplied to stage 1 through feed crystal supply line 34. In the experiments described hereinbelow the seed crystals were added batchwise about every thirty minutes.

The seed crystals were prepared from a solution of reagent grade phosphoric acid (85% H_3PO_4 , 61.6% P_2O_5 , and specific gravity of 1.7) which was quiescently cooled to a temperature between -5° and $-10^\circ C$ in plastic beakers. Upon adding one or

two crystals to the cooled acid, copious amounts of seed nuclei were rapidly formed, which formation was accelerated by vigorous agitation. The phosphoric acid nearly solidified within five seconds and then broke up into a thick seed slurry as agitation was continued. Agitation was continued for approximately one minute to break up lumps of seed crystals.

The seed slurry thus made usually contains 25% to 40% seed solids, depending upon the original acid strength and temperature prior to seed formation. The final temperature typically equilibrated between 15° and $25^\circ C$. The final seed size, measured by optical microscopy, was approximately 0.1 mm in length.

EXAMPLE 1

The crystallizer described above was employed to provide a three-stage cooling to crystals of primary crystallization at a temperature reaching $0^\circ C$ in stage 3.

The operating conditions for purposes of this experiment were:

Coolant: The coolant used to supply all three stages as well as the raffinate recycle drum was a 50% ethylene glycol-water mixture maintained at a temperature of approximately $-6^\circ C$.

Feed Acid: The feed acid was a concentrated wet-process phosphoric acid which had been clarified to remove solid impurities. The feed acid analyzed 60% P_2O_5 , 0.9% F, 1.7% Fe_2O_3 , 3.7% SO_4 , and contained less than 1% solids. It was supplied to stage 1 at $20^\circ C$ at a rate of 155 ml/min. In the feed tank the acid had a specific gravity of 1.85 and a viscosity of 180 cp.

Raffinate Recycle: Raffinate from previous runs had been accumulated in the raffinate cooling tank and cooled to a temperature of $2^\circ C$. The raffinate in this test had a specific gravity of 1.81 and a viscosity of about 1000 cp. It was supplied to stage 2 at a flow rate of 60 ml/min. and to stage 3 at a flow rate of 40 ml/min.

Seed Slurry: The seed slurry was prepared in 600 ml batches from furnace-grade acid having a specific gravity of 1.7 as described above. On batch was added to stage 1 each half hour. This amounts to an average of about 20 ml/min. of seed slurry, which in this test had a concentration between 25% and 41% solids.

Crystallizer Conditions: The three crystallizers were operated in the following conditions:

Conditions for Example 1

	<u>Stage 1</u>	<u>Stage 2</u>	<u>Stage 3</u>
Magma Temperature, °C	10	2	0
Coolant Flow, ml/min.	1150	1100	1200
Coolant Inlet Temperature, °C	-4	-4	-4
Coolant Exit Temperature, °C	2	-1	-3
% Solids Content.	40	38	36
Raffinate Feed Rate, ml/min	-	60	40
Magma Viscosity, 000's, cp	4-7	7-13	6-16
Specific Gravity.	1.90	1.89	1.88
Specific Heat.	0.354	0.262	0.317

Product Centrifugation : The product from the third stage of crystallization, which collected in vessel 7 at a temperature of 0°C, had a solids content of 36%. During centrifugation raffinate was removed at a rate of approximately 0.48 gallon/min.ft². The product had a cake density of 80 lbs/ft³. The presence of occluded raffinate in the filter cake tends to detract from the purity of the resultant product. While the filter cake can be washed with water, significant phosphoric acid losses can occur. Preferably, therefore, the centrifuged cake is washed with phosphoric acid. Melted primary crystals and/or furnace-grade acid can be used.

Using the foregoing conditions, a four-day run was carried out in which phosphoric acid was continuously crystallized. As indicated, the run was commenced by seeding cooled feed acid with a batch of furnace-grade seed crystals. The initial amount of seed corresponded to approximately 4 to 5% by weight of the feed acid. The periodic addition of seed crystals each half hour during the course of the run corresponded to between 3.4 and 5% by weight of the feed acid rate.

As the first stage filled, product therefrom was allowed to overflow into stage 2; and when stage 2 filled, the product overflowed to stage 3. Coolant rates in each of the stages 2 and 3 were set at 500 ml/min. as each stage filled. As indicated above, cooled, recycled raffinate was pumped at 60 and 40 ml/min., respectively, to stages 2 and 3 throughout the run in order to maintain a manageable solids content in each stage. A solids content of 30% to 38% appeared to be satisfactory.

Over a period of twelve hours of initial operation the coolant flows were gradually increased until an equilibrium temperature in stage 3 of 0°C was obtained. Thereafter coolant flows were held at 1100-1200 ml/min. At this time the solids contents and viscosities of stages 1, 2 and 3 were, respectively, 38% and 5300 cp., 36% and 7700 cp., and 34% and 9600 cp. Over the ensuing twenty four hours, the motor torques continued to increase until a steady state operation was achieved and the solids contents of the stages were not materially changing. At this time the solids content of stage 1 was 41%; that of stage 2 was 38%; and that of stage 3 was 36%. Viscosities, as indicated by the motor torques, had increased significantly to 7000, 13000 and 16000 cp. for the respective stages. The steady state solids content achieved in stage 3 was approximately 36%. This represented a P₂O₅ yield of 57% from the starting feed acid.

The product was centrifuged in a laboratory scale machine at 2100 rpm (876g's). During the centrifugation step the maximum raffinate rate was found to be approximately 0.48 gal/min ft². The finished product had a cake density of 80 lb/ft³. Initially the centrifuged cake contained approximately 65% P₂O₅ and 0.52% iron (as Fe₂O₃). Washing the centrifuged cake with ice cold water (5 gm water/100 gm cake) reduced the iron content to approximately 0.18%, although this resulted in a loss of approximately 33% of the cake weight. Washing with furnace-grade acid in an amount effective to provide about 5-10 grams of furnace-grade acid to 100 grams of cake was effective to reduce the iron content to as little as 0.16% while limiting the loss of cake to 13%. In another test the

cake was washed with melted primary cake (65% P_2O_5). This limited the cake loss to the same order of magnitude, but was somewhat less effective in reducing its iron content.

At the conclusion of the run seed crystal addition to stage 1 was discontinued, but feed acid continued to flow. Some three hours after the last seed addition the solid content from stage 3 has fallen from 36% to 23%. Over the next six hours solids content further declined to 4%. The temperature was held at 5°C throughout this period. This demonstrated that, in the present invention, the continuous crystallization process is not self-sustaining in the absence of continuous or intermittent seeding.

EXAMPLE 2

A further test of the present invention was made using a single stage of the three-stage crystallizer described above. One stage was filled with 2.25 gallons of fresh feed acid (60% P_2O_5) and 2.25 gallons of the raffinate from Example 1. The mixture was cooled to approximately 5°C and then seeded with 2200 grams of the same batch-prepared furnace acid seed slurry used in Example 1. This amounted to approximately 5% by weight seed based on fresh acid feed. Coolant flow in this test was initially maintained at 1100 ml/min., i.e., similar to the cooling rate used when each stage was run continuously. During the run, however, the coolant flow was gradually reduced as the magma approached 0°C at the conclusion of the six-hour run.

At the conclusion of the run the product was centrifuged to yield a cake having 85% P_2O_5 and 0.44% Fe_2O_3 . The net P_2O_5 from the phosphoric acid at 0°C calculated to be 60%.

EXAMPLE 3

In another test, batch crystallization was evaluated in a manner similar to that occurring in each successive stage of a continuous crystallizer. In this test a single stage in the three-stage crystallizer apparatus described above was employed.

Stage 1 of the crystallizer was initially filled with 4.5 gallons of 60% P_2O_5 wet-process phosphoric acid. The acid was cooled to about 4°C and seeded with 4483 grams of furnace-grade seed slurry prepared as described above. Coolant flow rate was maintained at 1100 ml/min.

When the solids content approached 35% approximately 1.16 gallons of magma were withdrawn and 1.24 gallons of raffinate from an earlier run were added. Later as the solids content again approached 35%, approximately 0.6 gallon of magma was withdrawn and replaced with approximately 0.7 gallon of additional cold raffinate. Throughout this time the temperature of the crystallizing magma decreased. As the temperature approached 0°C coolant flow rate was reduced so as to maintain that temperature at the conclusion of the run. After six hours the product was centrifuged to yield a cake having 64% P_2O_5 and 0.60% Fe_2O_3 . The raffinate was analyzed and found to contain 54% P_2O_5 and 2.72% Fe_2O_3 . The net P_2O_5 yield in this run was calculated to be 57%.

EXAMPLE 4

An experiment was carried out on a small scale using 1977 grams of 60% P_2O_5 wet-process phosphoric acid. The acid was first cooled to 10°C in a glass beaker; 139 grams of orthophosphoric acid hemihydrate seeds made from furnace acid, as above, and having an average length between 0.08 and 0.12 mm, were added to the wet-process acid. The resulting slurry was agitated at 60 rpm for 5-1/2 hours while maintaining the 10°C temperature by means of a cold bath. The magma formed at the end of the 5-1/2 hours was filtered in a glass frit, and the solids from the filtration were then centrifuged. The solids centrifuged thereby amounted to 652 grams of dry, well-defined, easy-to-separate crystals of $H_2PO_4 \cdot 1/2H_2O$ having the chemical composition of the hemihydrate product identified in Table I, above, and referred to as "Crystallized Product Cake". The amount of crystals obtained thereby represented a P_2O_5 yield of 29%.

EXAMPLE 5

The effect of fluoride content on purified, concentrated phosphoric acid yield is illustrated by the following tests which were carried out using a wet-process phosphoric acid having a concentration of about 61.8% P_2O_5 and which had been treated during manufacture to reduce the naturally occurring fluoride content to about 0.2%. The starting material for this series of tests had the following analysis:

in a batch crystallizer for about six hours at 0°C, with agitation at 125 rpm. Each sample was diluted with water or with aqueous solutions of hydrofluoric

20 Table II. Each batch was seeded with extra fine furnace-grade acid seed crystals in an amount equivalent to 5% of the weight of the feed acid.

The following results were observed:

TABLE VI

Results of Example 5

<u>Feed Analysis (%)</u>				<u>Magma</u>		<u>Yield</u>
<u>Test No.</u>	<u>P₂O₅</u>	<u>F</u>	<u>SO₄</u>	<u>% solids</u>	visc.	<u>(%)</u>
					(000's) <u>cp</u>	
A	60.9	0.20	4.31	36	28	65.6
B	60.8	0.88	4.29	39	34	79.4
C	60.0	0.20	4.24	31	14	57.4
D	60.0	0.86	4.23	36	24	66.0
E	59.9	1.73	4.22	36	13	67.8

The test results in Table VI clearly show that process yield is improved by increased concentrations of fluoride ion in the feed acid.

EXAMPLE 6

In more concentrated amounts the dilution effect of HF and fluosilicic becomes significant. Since dilution below about 60% P₂O₅ tends to reduce the yield of H₃PO₄•1/2H₂O, the addition of HF or H₂SiF₆ above around the 1% level does not normally result in increased yield relative to the yield obtain-

able from the original undiluted phosphoric acid. However the dilution has a substantial favorable effect on the magma viscosity. Thus, the addition of HF or H₂SiF₆ enables the yield level to be maintained, while operating in a more favorable viscosity region due to the greater amount of available water.

This effect is shown by the following test:

55 A large sample of magma was produced, equilibrated at 32°F and separated into aliquots to which various quantities of water, hydrofluoric acid, fluosilicic acid, and sulfuric acid were added. The

crystallizations were continued for a further nine hours, after which samples of raffinate were separated for analysis. Table VII illustrates the data generated. It can be seen that the addition of water, as expected, reduced the yield obtained. At the lower addition levels the presence of fluoride and sulfate ion both maintained the yield even though the system was not more dilute with respect to P_2O_5 .

A similar result was observed at the higher addition levels, with both fluoride and fluosilicate ions; similar yields, but thinner raffinates were obtained when compared with the 62% P_2O_5 control.

However, sulfuric acid addition gave a more viscous raffinate and lower yield. It was concluded that the addition of fluoride and fluosilicate ion allowed the system to be operated further into the wet region while maintaining yield, thus giving less viscous raffinates with consequent separational benefits.

In order to understand the role of the fluoride ion, a set of small scale experiments were carried out where various proportions of HF and water were added whilst maintaining the same net P_2O_5 strength. The results are shown in Table VII.

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TABLE VII
EFFECT OF ADDING LARGER AMOUNTS OF FLUORIDE

ORIGINAL FEED ACID % P ₂ O ₅	ADDITIVE	RESULTANT FEED STRENGTH % P ₂ O ₅	YIELD* INDEX	MAGMA VISCOSITY CP	% SOLIDS	RAFFINATE VISCOSITY CP (70°F)
62	0	62	41	114,000	29	2750
62	+1.6% H ₂ O	61	36	29,000	25	4600
62	+1.6% HF (50%)	61	44	64,000	37	1700
62	+1.6% H ₂ SO ₄	61	40	60,000	29	2600
62	+4.8% H ₂ O	59	31	900	15	900
62	+4.8% HF (50%)	59	42	60,000	31	620
62	+4.8% HF (50%)	59	41	13,600	33	700
62	+4.8% H ₂ SiF ₆ (25%)	59	40	13,600	34	1080
62	+4.8% H ₂ SO ₄	59	36	25,000	21	1800

$$\text{*Yield Index} = \frac{\% \text{ imp in feed} \quad \% \text{ P}_2\text{O}_5 \text{ in raffinate}}{\% \text{ P}_2\text{O}_5 \text{ in feed} \quad \% \text{ imp in raffinate}} \times$$

Claims

1. A method for purifying phosphoric acid containing impurities which interfere with crystallization, comprising

(i) adding to a vessel an aqueous solution of said impure phosphoric acid having a concentration such that, when cooled to a temperature between -10°C and $+25^{\circ}\text{C}$, said solution will be supersaturated with respect to $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$, in which vessel said phosphoric acid solution is maintained at a temperature at which it is supersaturated with respect to $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$, and dispersing seed crystals of orthophosphoric acid hemihydrate in said impure acid in an amount of at least 2% by weight of said impure phosphoric acid, and at a rate effective to substantially prevent said phosphoric acid from becoming a viscous, inseparable mass;

(ii) maintaining said phosphoric acid and seed crystals of orthophosphoric acid hemihydrate in said vessel at a temperature below super-saturation temperature for an nominal residence time sufficient to form a magma of crystallized $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$, having an average crystal size larger than that of the seed crystals and a liquid phase mother liquor containing the bulk of the impurities while controlling the temperature within said vessel to substantially prevent the occurrence of a viscous, inseparable mass; and

(iii) thereafter withdrawing said magma and separating said crystallized orthophosphoric acid hemihydrate from said liquid phase mother liquor.

2. A method for purifying phosphoric acid containing impurities which interfere with crystallization, comprising

(i) adding to a vessel an aqueous solution of said impure phosphoric acid having a concentration such that, when cooled to a temperature between -10°C and $+25^{\circ}\text{C}$, said solution will be supersaturated with respect to $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$, in which vessel said phosphoric acid solution is maintained at a temperature at which it is supersaturated with respect to $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$, and dispersing seed crystals of orthophosphoric acid hemihydrate in said impure acid in an amount of at least 2% by weight of said impure phosphoric acid, and at a rate effective to substantially prevent the occurrence of secondary nucleation in said phosphoric acid;

(ii) maintaining said phosphoric acid and seed crystals of orthophosphoric acid hemihydrate in said vessel at said temperature at which it is supersaturated to form a magma of crystallized $\text{H}_3\text{PO}_4 \cdot 1/2\text{H}_2\text{O}$ having an average crystal size larger than that of the seed crystals and a liquid phase mother liquor containing the bulk of the impurities

while controlling the temperature within said vessel to substantially prevent the occurrence of secondary nucleation; and

(iii) thereafter withdrawing said magma and separating said crystallized orthophosphoric acid hemihydrate from said liquid phase mother liquor.

3. The method according to claim 1 or 2 wherein said seed crystals of orthophosphoric acid hemihydrate are added in an amount of about 5% by weight of phosphoric acid.

4. A method according to claim 1 or 2 wherein said phosphoric acid has a P_2O_5 concentration of between about 58% and 63% by weight and a solids content of less than 3%.

5. A method according to claim 1 or 2 wherein said seed crystals have an average length of less than about 0.3 mm in diameter.

6. A method according to claim 1 or 2 wherein said seed crystals contain less than 0.1% iron calculated as Fe_2O_3 .

7. The method according to claim 1 or 2 wherein the crystallization is carried out in batches.

8. The method according to claim 1 or 2 wherein the crystallization is carried out continuously.

9. The method according to claim 1 or 2 wherein said separated crystallized orthophosphoric acid hemihydrate is recrystallized, and a further purified recrystallized product is separated.

10. A method for purifying wet-process phosphoric acid containing the impurities normally associated therewith, comprising

(i) adding to a crystallizer vessel wet-process phosphoric acid having a P_2O_5 concentration such that when cooled to a temperature between -10°C and $+25^{\circ}\text{C}$, said solution will be supersaturated with regard to orthophosphoric acid hemihydrate, said vessel containing a magma of crystallizing phosphoric acid hemihydrate derived from wet-process phosphoric acid, which vessel is maintained at a temperature at which the magma is supersaturated with respect to orthophosphoric acid hemihydrate;

(ii) adding seed crystals to said crystallizer vessel, while controlling the temperature in said crystallizer vessel to substantially prevent the occurrence of a viscous, inseparable mass, said seed crystals being dispersed in said crystallizer vessel in an amount of at least 2% by weight of the rate at which said wet-process phosphoric acid is added to said crystallizer vessel, the amount of said seed crystals, taken in conjunction with the frequency of the addition thereof and the rate at which they are dispersed in said magma, being effective to substantially prevent said phosphoric acid from becoming a viscous, inseparable mass;

crystallizer vessel, and

(iv) thereafter separating said crystallized orthophosphoric acid hemihydrate from said magma.

11. A method according to claim 10 wherein said crystallizer vessel comprises a plurality of successive stages in which

(i) fresh wet-process phosphoric acid is added to the first of said stages;

(ii) crystallized magma in said first stage is withdrawn to supply feed to the second of said stages, and each successive stage present is fed by magma from the immediately preceding stage; and

hemihydrate from said stages by centrifugation.

13. A method according to claim 10 wherein seed crystals have an average length of less than about 0.3.

10 14. A method according to claim 10 wherein said seed crystals contain less than 0.1% iron calculated as Fe_2O_3 .

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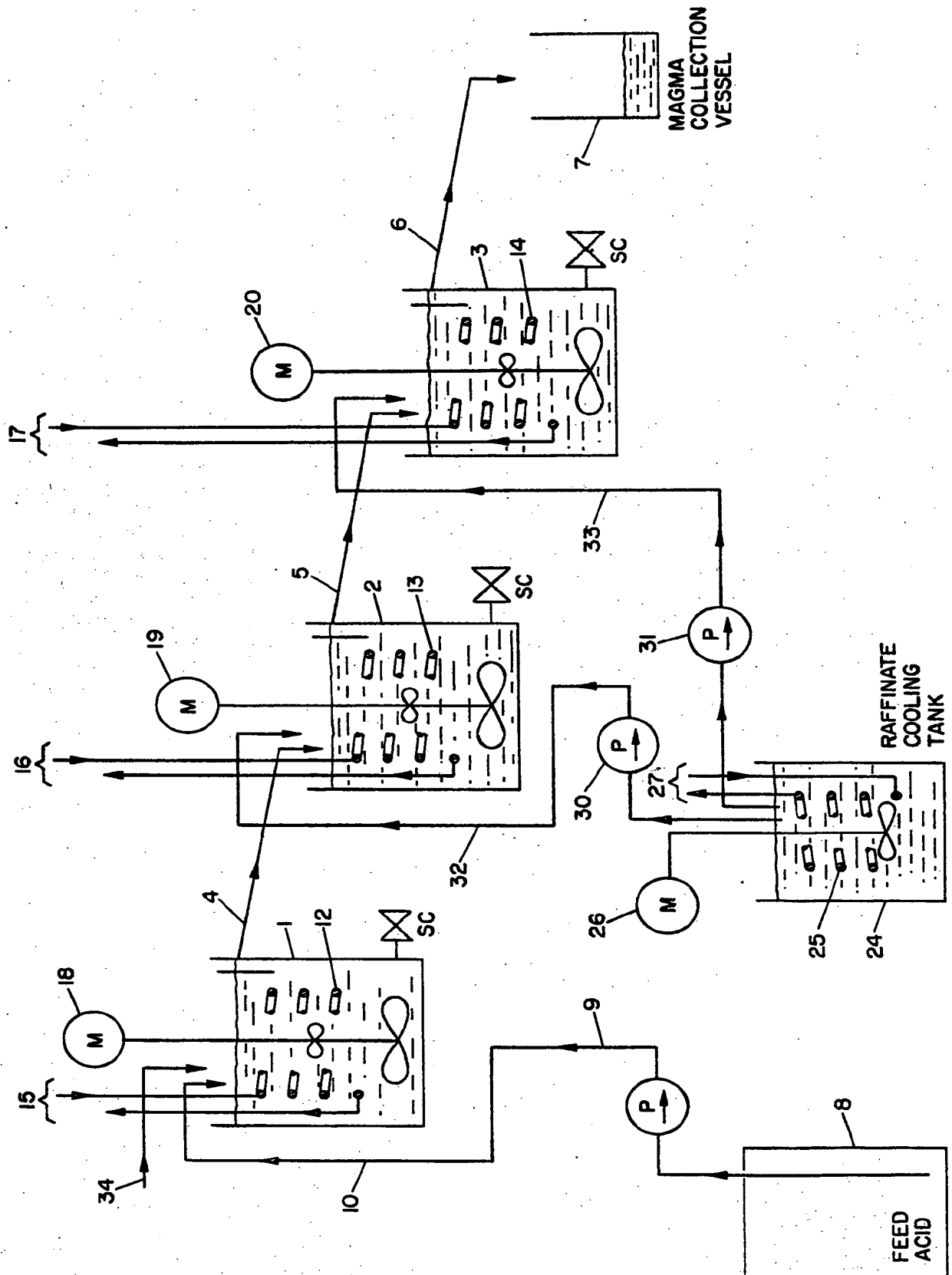
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	CHEMICAL ABSTRACTS, vol. 80, no. 26, 1st July 1974, page 69, abstract no. 147419d, Columbus, Ohio, US; & CS - A - 150 818 (P. STOPKA et al.) 15-10-1973		C 01 B 25/234
D,A	US-A-4 296 082 (E.J. LOWE et al.)		
A	GB-A-2 078 694 (ALBRIGHT & WILSON LTD.)		
A	CHEMICAL ABSTRACTS, vol. 77, no. 8, 21st August 1972, page 152, abstract no. 50841k, Columbus, Ohio, US; J. SKRIVANEK et al.: "Effect of temperature fluctuations on the shape and purity of orthophosphoric acid semihydrate crystals"		
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 01 B 25/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-08-1986	Examiner BREBION J.CH.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	